

TRANSLATION:

(19) Japanese Patent Office (JP)

(11) Kokai No.: 3[1991]-44,354

(12) Kokai Patent Gazette (A)

(43) Kokai Date: February 26, 1991

EARLY DISCLOSURE
[Unexamined Patent Application]

(51) Intl. Cl.⁵:

C 07 C 69/96

B 01 J 27/232

C 07 C 68/06

//C 07 B 61/00

Identification Code:

Z

A

300

Office Ref.:

6516-4H

6516-4H

No Examination Requested

Number of Claims: 1 (total: 5 pages)

(54) Title of the Invention:

METHOD FOR THE PRODUCTION OF DIALKYL CARBONATES

(21) Application No.:

1[1989]-178,348

(22) Application Date:

July 11, 1989

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S P E C I F I C A T I O N

1. Title of the Invention

METHOD FOR THE PRODUCTION OF DIALKYL CARBONATES

2. Scope of the Patent Claim(s):

Method for the production of dialkyl carbonates, characterized in that,

when producing a dialkyl carbonate from an alkylene carbonate and an aliphatic alcohol, a hydrotalcite compound that contains at least both MgO and Al_2O_3 is used as the catalyst.

3. Detailed Description of the Invention

Field of Industrial Application

The present invention pertains to a method for the production of dialkyl carbonates.

In more detail, the present invention pertains to a method for the production of dialkyl carbonates from alkylene carbonates and aliphatic alcohols and, in particular, to a method characterized in that a hydrotalcite inorganic compound that contains at least both MgO and Al_2O_3 is used as the catalyst.

Solvents for various materials such as resins and paints, and alkylating agents are known industrial applications for dialkyl carbonates that are produced.

Furthermore, it is known that dialkyl carbonates will react with amines to form carbamates.

Conventional Technology

The following three processes are widely known methods for the production of dialkyl carbonates.

In one process, dialkyl carbonates are produced by the reaction of phosgene with alcohol, and known methods of this kind are disclosed in Japanese Kokoku No. 62[1987]-853,500, Japanese Kokai No. 60[1985]-197,639, and Japanese Kokai No. 61[1986]-118,349. These methods use extremely toxic phosgene and

thus involve considerable danger as well as the unwanted co-production of large amounts of hydrogen chloride.

In another process, dialkyl carbonates are produced by the reaction of carbon monoxide with an alcohol, and known methods like this are disclosed in Japanese Kokoku No. 60[1985]-58,739, Japanese Kokoku No. 56[1981]-8,020, Japanese Kokoku No. 60[1985]-23,662, and Japanese Kokoku No. 61[1986]-8,816.

These methods use highly toxic carbon monoxide and thus pose considerable risks. Another shortcoming is the co-production of water, which simultaneously hydrolyzes the dialkyl carbonates as they are produced.

In yet another process, dialkyl carbonates are produced by the reaction of alkylene carbonates with an alcohol, and known methods like this are disclosed in Japanese Kokoku No. 60[1985]-22,698, Japanese Kokoku No. 60[1985]-4,381, Japanese Kokoku No. 60[1985]-22,697, Japanese Kokoku No. 56[1981]-40,708, Japanese Kokoku No. 61[1986]-16,267, Japanese Kokoku No. 60[1985]-27,658, and Japanese Kokoku No. 59[1984]-28,542.

These latter methods have an advantage in that they do not use toxic compounds such as phosgene and carbon monoxide. Another feature of these latter methods is the co-production of alkylene glycols that correspond to the alkylene carbonates. Moreover, the manufacturing cost of the dialkyl carbonates can be substantially reduced by selling these co-produced alkylene glycols.

Problems to be Solved by the Invention

Problems associated with the method of producing dialkyl carbonates by the reaction of alkylene carbonates with lower aliphatic alcohols include the following:

Alkylene carbonates undergo decomposition or polymerization if exposed to

high temperatures (for example, 200°C or more) in the presence of an ester interchange catalyst.

Because of this, when the catalyst is dissolved in the reaction system, the alkylene carbonate can be lost in a purification system.

However, many of the catalysts described in the aforementioned patents are soluble in crude reaction solution under the reaction conditions, and can not be separated easily from the reaction solution that forms, so in many cases they end up as obstacles when trying to develop continuous operation of the reaction as an industrial process.

In some limited areas, synthetic zeolites and organic ion exchange resins are used in the reaction as solid-acid and solid-base catalysts that do not dissolve in the reaction solution and can thus be separated easily after the reaction. Unfortunately, however, from the standpoint of activity, life, preparation, handling ease, and economics, these catalysts are not altogether satisfactory for use in the reaction of the present invention.

The present inventor and others conducted various investigations to find effective catalysts for the production of dialkyl carbonates from alkylene carbonates and aliphatic alcohols, and as a result of these investigations, it was discovered that various excellent advantages are made possible when a hydrotalcite compound that contains at least both MgO and Al_2O_3 is used as the catalyst.

~~The greatest advantage of all is the fact that said catalyst is insoluble~~
in the crude reaction solution.

Because of this, the catalyst can be kept out of the purification system, thus making the loss of alkylene carbonate in the purification system essentially zero.

Furthermore, the crude reaction solution can be purified by batch distillation, which sharply reduces the cost of the facility.

Constitution of the Invention

In other words, the present invention comprises "a method for the production of dialkyl carbonates, characterized in that, when producing a dialkyl carbonate from an alkylene carbonate and an aliphatic alcohol, a hydrotalcite compound that contains at least both MgO and Al_2O_3 is used as the catalyst".

The method for the production of dialkyl carbonates of the present invention will now be described in more detail.

The main feature of the present invention is that hydrotalcite compounds, which have previously been used as clarifying agents for various liquid compounds, are used as the catalysts. In particular, hydrotalcite compounds that contain both MgO and Al_2O_3 are used.

It is well known that hydrotalcite compounds are highly adsorptive for alkalis, acids, halogen ions, and metal ions.

The mechanism of clarification when they are used as clarifying agents/-decolorants for liquid compounds is thought to be related to this adsorptive power, but the present inventor focussed his attention on the use of these compounds as a catalyst.

The catalyst to be used in the production method of the present invention must be a hydrotalcite compound that contains at least both MgO and Al_2O_3 .

A hydrotalcite compound is a generic term for hydrated basic carbonate minerals of Mg and Al . Various grades of these products that depend on differences in the main components are available commercially.

(1) $2.5\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (trade name Kyowaad 300)

(2) $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ (trade name Kyowaad 500)

(3) $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}\text{CO}_3 \cdot m\text{H}_2\text{O}$ (trade name Kyowaad 1000, $m = 3-3.5$)

(4) $\text{Mg}_{0.7}\text{Al}_{0.3}\text{O}_{1.15}$ (trade name Kyowaad 2000) in a form such that about 30 mole% of Al_2O_3 is dissolved in MgO .

In the present invention, these catalysts are used in amounts of at least 0.1 weight% or more, and preferably 1 weight% or more, based on the total weight of the alkylene carbonate in the case of a batch reaction, and the larger the amount, the more effective is the catalyst.

As a matter of course, however, there is a limit to the catalytic effect corresponding to the amount added, and the correct amount should be about 5-20 weight%, considering the cost-to-effect ratio. There are no particular limitations on the particle size of the catalyst used. For example, whether a fine powder that passes thru 20-mesh or more or formed granules with a diameter of about 3 mm are used, there is not much difference in the catalytic effect.

Furthermore, when using a granular or pellet-form hydrotalcite compound, continuous processing is possible by packing it in a fixed bed.

In the case of a batch reaction, there are no particular limitations on the order of adding the starting materials and the catalyst, but in order to allow the catalyst to disperse fully in the mixed solution, it works best when at least one of the starting materials is added first, followed by the catalyst with stirring.

A hydrotalcite compound that contains both MgO and Al_2O_3 and which is used in the method for the production of dialkyl carbonates in accordance with the present invention, has both good activity and selectivity. The catalytic effect produced is as good as that of an effective Lewis acid catalyst, which

is the type of catalyst that has generally been used in production methods of this kind.

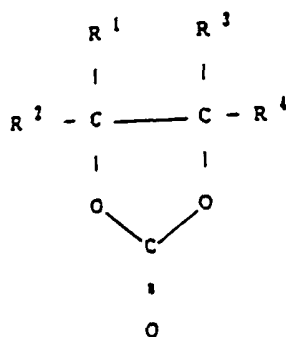
On the other hand, the invention catalyst is insoluble in the reaction solution that contains the starting materials and the products, which provides an advantage in that it can be easily separated and recovered from the reaction solution after completion of the reaction.

Furthermore, the catalyst activity of these catalysts lasts a long time, which results in greater stability with practically no loss of activity, even after lengthy continuous operations.

The reaction temperature will differ, depending on the type of carbonate starting material, the type of catalyst, and the composition of the reaction solution at the start of the reaction, i.e., no one temperature works well under all conditions. In general, though, the temperature is in the range of 100-300°C, and preferably 120-200°C. Higher temperatures will result in faster reaction rates.

The crystalline inorganic anion exchanger used as the catalyst in the production method of the present invention has better heat resistance than organic ion exchange resins which are similar solid base catalysts, particularly anion exchange resins based on styrene-divinylbenzene copolymers. It is also very stable under the reaction conditions, which means that the reaction temperature will not be limited by the thermal stability of the catalyst, as in the case of ion exchange resins.

A suitable alkylene carbonate for use as one of the starting materials can be represented by the following general formula



(in which R^1 , R^2 , R^3 , and R^4 represent hydrogen, an alkyl group, an aryl group, an alkenyl group, or a cycloalkyl group).

Specific examples include lower alkylene cyclic carbonates such as ethylene carbonate, propylene carbonate, 1,2-butylene carbonate, and 2,3-butylene carbonate, but ethylene carbonate and propylene carbonate work especially well.

The ethylene carbonate is in the form of colorless, odorless crystals with a boiling point of 100°C (100 mm Hg) and a melting point of 39°C . It can be produced industrially by reacting ethylene oxide and carbon dioxide at a high temperature and high pressure in the presence of a catalyst. Propylene carbonate is a colorless, odorless liquid with little corrosiveness and moisture absorption, a boiling point of 241.7°C , and a melting point of -49.2°C . It can be produced industrially by reacting propylene oxide and carbon dioxide at a high temperature and high pressure in the presence of a catalyst.

Both ethylene carbonate and propylene carbonate are highly soluble in polymer products such as nylon, polyacrylonitrile, cellulose-based resins, and bisphenol-based resins. What is more, they are compatible with plasticizers and mix well with general solvents, and thus are used as solvents.

Furthermore, propylene carbonate is a colorless, odorless liquid with

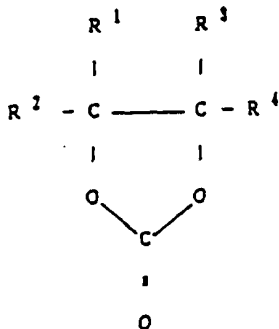
little corrosiveness and moisture absorption, and with a melting point of -49.2°C , which is widely used as an intermediate in the formation of carbamates, as a hydroxypropylating agent, or as a starting material for the production of pharmaceuticals, agrochemicals, and surfactants by ester interchange. It is synthesized industrially by reacting propylene oxide and carbon dioxide at a high temperature and high pressure in the presence of a catalyst.

Dialkyl carbonates, which are the main target compounds of the invention method, can be used as solvents for various materials such as resins and paints, or as alkylating agents, as mentioned previously.

Furthermore, dialkyl carbonates form carbamates by reacting with amines, and the use of carbamates to produce diisocyanate compounds by thermal decomposition is well known.

A suitable aliphatic alcohol for use as one of the starting materials can be an alcohol with a number of carbon atoms in the range of 1 to 10. Specific examples include lower aliphatic alcohols such as methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol, *sec*-butanol, and *tert*-butanol; middle alcohols such as pentanol, heptanol, hexanol, octanol, decanol, and their isomers; and alkoxy-substituted lower alcohols such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol mono(*n*- or *iso*)propyl ether, ethylene glycol mono(*n*-, *iso*-, *sec*- or *tert*-)butyl ether, propylene glycol, or monomethyl ether, monoethyl ether, mono(*n*- or *iso*)propyl ether, and mono(*n*-, *iso*-, *sec*- or *tert*-)butyl ether of 1,4-butanediol.

The alkylene glycol which forms as a by-product in the production method of the present invention can be represented by the general formula:



(in which R^1 , R^2 , R^3 , and R^4 represent hydrogen, an alkyl group, an aryl group, an alkenyl group or a cycloalkyl group).

When the alkylene glycol, to be produced is ethylene glycol, ethylene carbonate should be used as the alkylene carbonate; when propylene glycol is to be produced, propylene carbonate should be used as the alkylene carbonate.

According to 1987 domestic demand, with regard to the use of the co-produced alkylene glycol, for ethylene glycol, the fields of fibers and films account for about 60% of the domestic demand and the fields of antifreezes, unsaturated polyester resins, alkyd resins, and others account for the rest. In the case of propylene glycol, the industrial grade product is used in unsaturated polyester resins, etc., and the limited food grade product is used in toothpaste, cosmetics, medicines, tobacco, foods, flavors, etc.

The molar ratio of aliphatic alcohol to alkylene carbonate starting material is theoretically 2, but can be selected as desired.

Furthermore, depending on the composition of the reaction solution, the boiling point is reached below the desired temperature at standard pressure (i.e., open to the atmosphere), and the expected reaction rate may not be attained in some cases.

In cases of this kind, a pressure reactor can be used and the reaction can be carried out without actually applying any pressure, i.e., only the

pressure that develops when the reaction solution is heated to the desired temperature is used. Another possibility is to raise the boiling point with the use of an appropriate solvent, or a step can be introduced where an appropriate gas is added to the system under pressure.

The solvent used should be stable under the reaction conditions, and should not react with the reaction mixture of the starting materials and catalyst. Furthermore, it should not react with the products, nor decompose. In general, however, any solvent can be used as long as it has an acceptable affinity for the reaction mixture and has an appropriate boiling point.

Furthermore, there are no particular limitations with regard to the gas to be used, other than the fact that it must be an inert gas.

The pressure in the reactor may be adjusted as appropriate, if needed, and does not necessarily need to be kept constant during the course of the reaction.

Moreover, the reactor material can be chosen mainly by the corrosiveness of the catalyst, since not much corrosion is anticipated with most of the reaction starting materials and reaction products of the present invention.

A dialkyl carbonate of high purity can easily be obtained from the reaction mixture in accordance with the production method of the present invention. This can be done by an operation such as distillation, using the reaction mixture as-is, or after removing the catalyst by filtration or centrifugation, or after the catalyst is made chemically inactive (including separation).

The method of the present invention is carried out under liquid-phase conditions, but the reaction mode is not particularly critical. For example, any mode such as batch, semi-continuous, and continuous can be used.

Typical reaction examples will now be given to better describe the method of the present invention. It goes without saying, however, that these examples are merely illustrative, and are in no way to be interpreted as limiting the scope of the present invention.

Actual Example 1

162.6 g of methanol, 407.8 g of propylene carbonate, 18.1 g of dimethyl carbonate, and 30.98 g of $\text{Mg}_{0.7}\text{Al}_{0.3}\text{O}_{1.15}$ (trade name Kyowaad 2000 and manufactured by Kyowa Gas Chemical Industries) as the catalyst were introduced into a 1-L autoclave made of SUS316 and equipped with a thermometer and a stirrer. The reaction was conducted for 8 hours at 160°C and at a pressure of 3 kg/cm².

After completion of the reaction, the crude reaction solution was taken out at room temperature and atmospheric pressure and analyzed by gas chromatography, which revealed a content of 19.6 wt.% methanol, 12.2 wt.% dimethyl carbonate, 7.9 wt.% propylene glycol, and 55.3 wt.% propylene carbonate.

The selectivity of propylene carbonate for dimethyl carbonate was 99% or more.

Actual Example 2

The method of operation was similar to that of Actual Example 1, except that 351.8 g of ethylene carbonate was used in place of propylene carbonate.

The selectivity of ethylene carbonate for dimethyl carbonate was 99% or more.

Actual Example 3

The method of operation was similar to that of Actual Example 1, except that 233.7 g of ethanol was used in place of methanol.

The selectivity of propylene carbonate for dimethyl carbonate was 99% or more.

Applicant: Daicel Chemical Industries Co., Ltd.
